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DISPERSION OF MICROWAVES IN OXYGEN

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ABSTRACT. Dispersion of microwaves has been theoretically calculated in the case of gaseous oxygen on the basis of Van Vleck-Weisskopf expressions for the collision broadened microwave spectral lines. Curves are plotted at pressures of $\frac{1}{4}$, 1, 2, 10, 25 and 50 atmospheres in a wide frequency band both for resonant and nonresonant cases. The calculated value of static magnetic susceptibility agrees with the known experimental value.

INTRODUCTION

Oxygen molecule presents an interesting case in the microwave region. The molecule is electrically nonpolar and the absorption and dispersion of microwaves is attributed to it being magnetically polar. Analysis of the band spectrum has shown that oxygen molecule has a $^3\Sigma$ ground state. It has the spin quantum number unity and the Lande g factor two and, hence, the molecule has the magnetic dipole moment of 2 Bohr magnetons ; which interacts with the 'end over end' rotation of the molecule to form a 'rho type triplet'. The resolved fine structure of the microwave spectrum has been studied by a number of workers in the vicinity of 60 kMcps.[1,2]. The transitions involved here are between $J = K$ and $J = K-1$ (negative transition) and $J = K$ and $J = K+1$ (positive transitions). Selection rule prohibits the transition between $J = K-1$ and $J = K+1$. These states nearly coincide and differ from $J = K$ by about 2 cm^{-1} and hence all the lines are clustered about 2 cm^{-1}. There is, however, a subsidiary resonance at 4 cm^{-1} involving the single transition $J = K$ to $J = K-1$ for $K = 1$. In addition to this resonance absorption, oxygen molecule also shows a nonresonant or Debye type of absorption and dispersion which is attributed to the diagonal part of the matrix element of the magnetic moment i.e. projection of the Spin vector S parallel to the resultant angular moment vector J about which S precesses. On the average it is found that one third of the total mean squared moment is of the diagonal variety while the other two third being consumed by the nondiagonal type of absorption i.e. the resonance absorption. The study of the resolved oxygen spectrum in the low pressure has shown about 29 absorption lines. The measurement of the line width parameter (Artman, 1953) has shown that it is very nearly constant for all the lines. At a higher pressure, all the lines merge to form a single broad line with centroid frequency at 2 cm^{-1}. An average value of the line width parameter weighted for line intensity has been found to

be 1.94 Mc/mm Hg. In case of air, allowing for difference in collision cross section between oxygen and air, the average value is 18% lower i.e. 0.039 cm^{-1}/atm. The value of the line width parameter for the 'nonresonant' line at zero frequency is still uncertain for lack of any experimental absorption data at wavelengths above 1 cm. Van Vleck (1947) predicted the attenuation offered by oxygen in the millimeter region due to the nonresonant line taking two likely values of the line width parameter i.e. $\Delta\bar{\nu} = 0.02$ and $0.05\ cm^{-1}$/atmos. the former being the most probable value and the latter being the upper limit.

CALCULATIONS

Van Vleck's and later Artman's calculations predicting the amount of attenuation offered by oxygen in the mm region at atmospheric pressure of air were based on the quantum mechanical expressions of Van Vleck and Weisskopf (1945) for the collision broadened microwave spectral lines. The expression for the absorption coefficient is:

$$\frac{\alpha'}{\bar{\nu}^2} = \frac{4\pi^2 \Sigma N_{ij} |\mu_{ij}|^2}{3kT} \left[\frac{\Delta\bar{\nu}^2}{\Delta\nu^2 + (\bar{\nu}+\bar{\nu}_0)^2} + \frac{\Delta\nu^2}{\Delta\bar{\nu}^2 + (\bar{\nu}-\bar{\nu}_0)^2} \right] \quad \ldots (1)$$

$$= 2\pi I.p \left[\frac{\Delta\bar{\nu}^2}{\Delta\bar{\nu}^2 + (\bar{\nu}+\bar{\nu}_0)^2} + \frac{\Delta\bar{\nu}^2}{\Delta\bar{\nu}^2 + (\bar{\nu}-\bar{\nu}_0)^2} \right] \quad \ldots (2)$$

where α is the absorption coefficient (per cm); $\bar{\nu}$ is the frequency (cm^{-1}); $\bar{\nu}_0$ is the resonance frequency; $\Delta\bar{\nu}$ is the line width parameter (cm^{-1}); I is the intensity factor and p is the pressure in cm of Hg.

The contribution of the nonresonant line with the line width parameter $\Delta\bar{\nu}_0$ to the absorption at a frequency $\bar{\nu}$ is obtained by putting $\bar{\nu}_0 = 0$ and using half the value of $I.p$, since one third of the squared moment contributes to the nonresonant absorption while two thirds to the resonant absorption, in the expression (2) above:

$$\frac{\alpha''}{\bar{\nu}^2} = 2\pi \left(\frac{I.p}{2} \right) \left[\frac{2\Delta\bar{\nu}^2_0}{\Delta\bar{\nu}^2_0 + \bar{\nu}^2} \right] \quad \ldots (3)$$

$$= 2\pi\ I.p[\Delta\bar{\nu}^2_0/(\Delta\bar{\nu}^2_0 + \bar{\nu}^2)]$$

Hence the net absorption at a frequency comes out to be:

$$\frac{\alpha}{\bar{\nu}^2} = \frac{\alpha'+\alpha''}{\bar{\nu}^2} = 2\pi I.p \left[\frac{\Delta\bar{\nu}^2}{\Delta\nu^2 + (\bar{\nu}+\bar{\nu}_0)^2} + \frac{\Delta\bar{\nu}^2}{\Delta\bar{\nu}^2 + (\bar{\nu}-\bar{\nu}_0)^2} + \frac{\Delta\nu^2_0}{\Delta\nu_0 + \nu^2} \right] \ldots (4)$$

The associated dispersion of the microwaves due to the magnetic dipole moment can be calculated by the quantum mechanical Van Vleck-Weisskopf expression

for dispersion. The case is parallel to the calculation of the electric susceptibility in ND_3 by the author (1956). In this case the magnetic susceptibility $(\mu'-1)$ or δ_m at a frequency $\bar{\nu}$ due to a resonance line at $\bar{\nu}_0$ of line width parameter $\overline{\Delta\nu}$

$$\delta_m'' = I.p\left[\frac{\overline{\Delta\nu}^2+\bar{\nu}_0(\bar{\nu}+\bar{\nu}_0)}{\Delta\nu^2+(\bar{\nu}+\bar{\nu}_0)^2}+\frac{\overline{\Delta\nu}^2-\bar{\nu}_0(\bar{\nu}-\bar{\nu}_0)}{\overline{\Delta\nu}^2+(\bar{\nu}-\bar{\nu}_0)^2}\right] \quad \ldots (5)$$

$$= I.p.S \quad \ldots (6)$$

where S is the shape function. The expression for the contribution of the Debye line at zero frequency to the net susceptibility at a frequency $\bar{\nu}(cm^{-1})$ with the line width parameter $\Delta\bar{\nu}_0$ is obtained by putting $\bar{\nu}_0 = 0$ and taking half the value of $I.p.$ in the expression (5) above. The expression is:

$$\delta_m' = \frac{I.p}{2}\left[\frac{2\overline{\Delta\nu_0}^2}{\overline{\Delta\nu_0}^2+\bar{\nu}^2}\right] \quad \ldots (7)$$

Hence the net value of the magnetic susceptibility at a frequency $\bar{\nu}$ taking into account the contributions of the nonresonant and resonant lines is:

$$\delta_m = \delta'_m+\delta''_m = I.P.\left[\frac{\overline{\Delta\nu}^2+\bar{\nu}_0(\bar{\nu}+\bar{\nu}_0)}{\overline{\Delta\nu}^2+(\bar{\nu}+\bar{\nu}_0)^2}+\frac{\overline{\Delta\nu}^2-\bar{\nu}(\bar{\nu}_0-\bar{\nu}_0)}{\overline{\Delta\nu}^2+(\bar{\nu}-\bar{\nu}_0)^2}+\frac{\overline{\Delta\nu^2}_0}{\overline{\Delta\nu}^2+\bar{\nu}^2_0}\right] \ldots (8)$$

The values of $I.p.$ have been calculated at different pressures (Maryott and Birnbam, 1955) and tabulated in Table I.

TABLE I

Values of intensity factor at different pressures and at 20°C

	Pressure in Atmospheres			
	1	2	25	50
$I.p\times10^6$	0.59	1.19	14.89	29.77

DISPERSION NEAR 2CM^{-1}

The dispersion curves have been calculated for the individual lines at $\frac{1}{4}$ atmospheric pressure where most of the lines are resolved and for the pressure broadened envelope at higher pressures. The value of the line width parameter has been taken to be 1.94 Mc/mm Hg and its variation with pressure has been assumed to be linear. Table II gives the various frequencies of transitions (Artman 1953 and Burkhalter *et al.*, 1950) together with their relative intensities. The intensities have been calculated by the following formulae:

$$(I.\overline{\Delta\nu})_- = 2.917\times10^{-14}\,\frac{(\upsilon_{k-})^2(K+1)(2K-1)}{T^3\,K}\exp\left[-\frac{2.072K(K+1)}{T}\right]\frac{10^{-6}cm^{-1}\,MC}{mmHg}$$

$$(I.\bar{\Delta}\nu)_+ = 2.917\times10^{-14}\ \frac{(\nu_{k+})^2}{T^3}\ \frac{K(2K+3)}{K+1}\ \exp\left[-\frac{2.072K(K+1)}{T}\right]\cdot\frac{10^{-6}\text{cm}^{-1}MC}{\text{mm Hg}}$$

The value of $(I.\bar{\Delta}\nu)$ for the most intense transition $J = 9$ to $J = 10$ is 41.01×10^{-6} cm^{-1} Mc/mm Hg. Fig. 1 shows the complex dispersion pattern calculated at

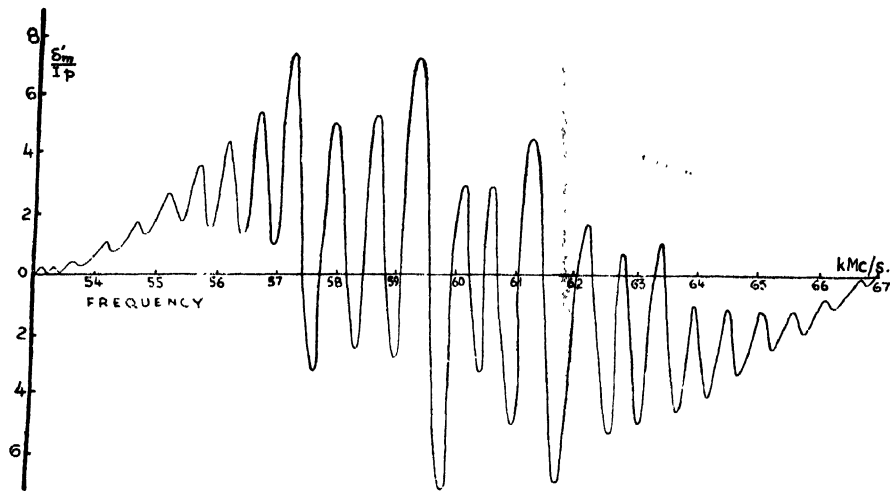

Fig. 1. Dispersion curves of oxygen at .25 atmospheric pressure in the 2 cm^{-1} region.

a pressure of $\frac{1}{4}$ atmosphere for individual lines and then added up for all the lines. The relative intensities of the absorption lines are given in Table II. The lines lose their individuality at higher pressures and hence the curves drawn in Fig. 2 at pressures of 1, 10, 25, 50 atmosphere show single broad dispersion curves due

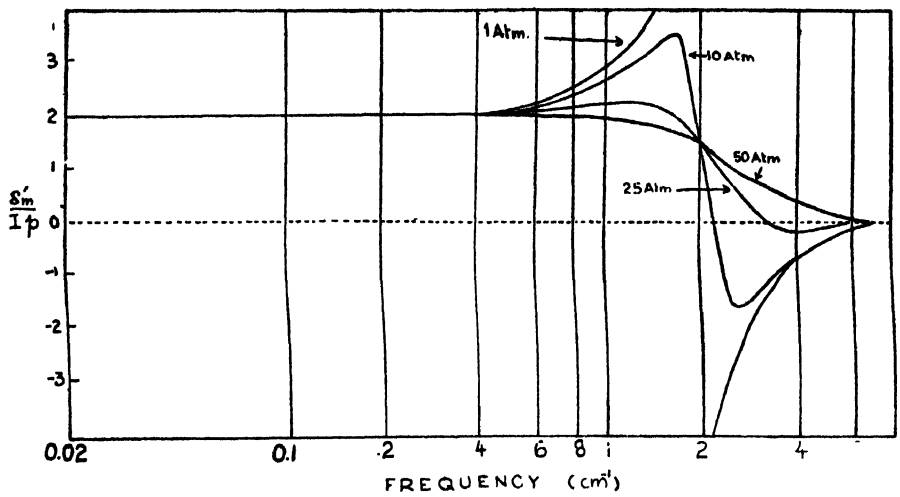

Fig. 2. Dispersion curves of oxygen at 1,10,25 and 50 atmospheric pressure in the wide frequency band due to the resonance line at 2 cm^{-1}.

to the envelope. It is observed that in case of oxygen low pressure conditions prevail even at one atmosphere pressure because of its small collision diameter (~ 4 Å) as compared to the average distance between the molecules (~30 Å).

TABLE II

	Negative transitions $J = K \rightarrow J = K-1$		Positive transitions $J = K \rightarrow J = K+1$	
K	Frequency	Intensity	Frequency	Intensity
1	118.750 kMc/s	0.732	56.265 kMc/s	0.205
3	62.486	0.631	58.446	0.560
5	60.306	0.840	59.592	0.823
7	59.163	0.930	60.435	0.972
9	58.324	0.909	61.152	1.000
11	57.612	0.804	61.800	0.926
13	56.969	0.654	62.412	0.796
15	56.363	0.492	62.998	0.616
17	55.784	0.348	63.568	0.447
19	55.221	0.226	64.128	0.356
21	54.673	0.139	64.679	0.194
23	54.130	0.080	65.223	0.116
25	53.592	0.043	65.762	0.065
27	53.066	0.022	66.296	0.034
29	×		66.828	0.017

DEBYE DISPERSION

Contribution to the magnetic susceptibility of the gas by the diagonal component of the matrix element magnetic dipole moment has been calculated on the basis of expression (7). Since the exact value of $\overline{\Delta\nu}_0$ is still not known, dispersion curves are plotted in Fig. 3 for the value of $\overline{\Delta\nu}_0 = 0.02$ cm^{-1}/atmosphere at pressures of 1, 2, 20 and 50 atmospheres. The dispersion is very sharp at low pressures and as the pressure is increased, it broadens and extends to the higher frequency region.

The net value of the magnetic susceptibility of the gas can be obtained by adding the two component values from the graphs or calculating it from the general

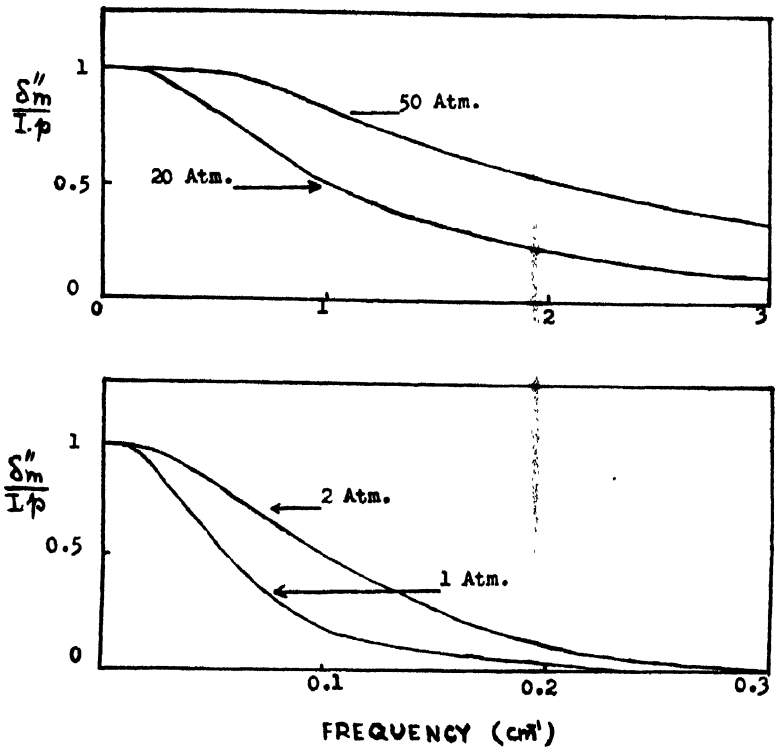

Fig. 3. Dispersion curves of oxygen at 1, 2,20 and 50 atmospheric pressure in the wide frequency band due to the nonresonant or Debye line at zero frequency.

expression (8). The value of static magnetic susceptibility at one atmospheric pressure and 20°C comes out to be :

$$(\mu' - 1)_0 = \delta'_{m0} + \delta''_{m0}$$
$$= 3\, I.p = 1.78 \times 10^{-6}.$$

This value compares very well with the value of $(\mu' - 1)$ as 1.8×10^{-6} quoted by Birnbaum *et al* (1951). More experimental work specially at higher wavelengths is needed in this direction.

REFERENCES

Artman, J. O., 1953 Columbia Rad. Lab. Report, June 1.

Birnbaum, G., S. J. Kryder and H. Lyons, 1951, *J. Appl. Phys.*, **22**, 95.

J. H. Burkhalter, R. S. Anderson, W. V. Smith and W. Gordy, 1950, *Phys. Rev.* **79**, 651.

Maryott, A. A. and Birnbaum, 1955, G., *Phys. Rev.*, **99**, 1886.

Prem Swarup, 1956, *Phys. Rev.*, **104**, 89.

Townes, C. H. and Schawlow, A. L. 1955, Microwave Spectroscopy (McGraw Hill).

Van Vleck, J. H., 1947, *Phys. Rev.*, **71**, 413.

Van Vleck, J. H. and Weisskopf, V. F., 1945, *Rev. Mod. Phys.*, **17**, 227.